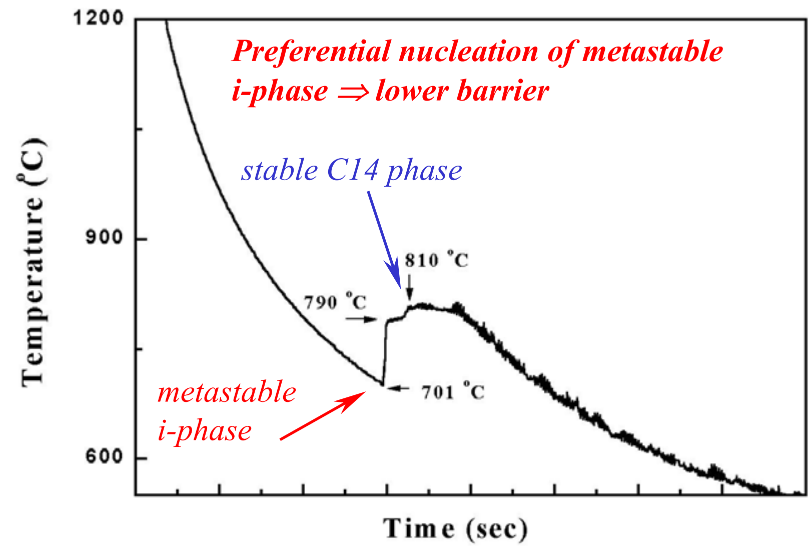
Structural and Microstructural Studies of Ti/Zr and Al-Based Quasicrystals, Approximants, and Metallic Glasses

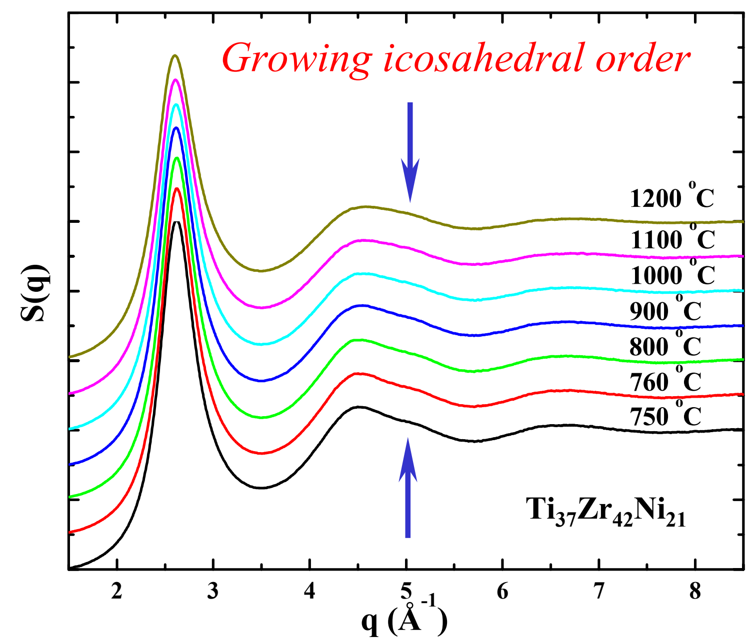
Kenneth F. Kelton, Washington University, St. Louis, DMR - 0307410

Icosahedral order and nucleation barrier - Proof of a half-century-old hypothesis -

With additional partial support from NASA NAG 8-1682, working with J. Rogers, NASA, MSFC, and D. Robinson, μ-CAT at the Advanced Photon Source, we demonstrated growing icosahedral order and the preferential nucleation of a metastable icosahedral phase. This confirms a hypothesis made by Charles Frank over 50 years ago, that the nucleation barrier for liquid metals is due to local icosahedral order in the liquid.



Electrostatically levitated droplet of a TiZrNi liquid using ESL facility at NASA Marshall Space Flight Center (MSFC)



K. F. Kelton et al., Phys. Rev. Lett. 90, 195504-1 (2003)

Structural and Microstructural Studies of Ti/Zr and Al-Based Quasicrystals, Approximants, and Metallic Glasses

Kenneth F. Kelton, Washington University, St. Louis, DMR - 0307410

Education:

Three undergraduates (David Lucy, Michael George and Josiah Hartzell), two graduate students (Van Huett and Youtao Shen), and one postdoc (Li Qian Xing) are supported by this grant. Studies of phase formation in TiZrHfNi alloys (figure to right), a potential new hydrogen storage material, were largely carried out by Josiah Hartzell as part of his senior thesis project

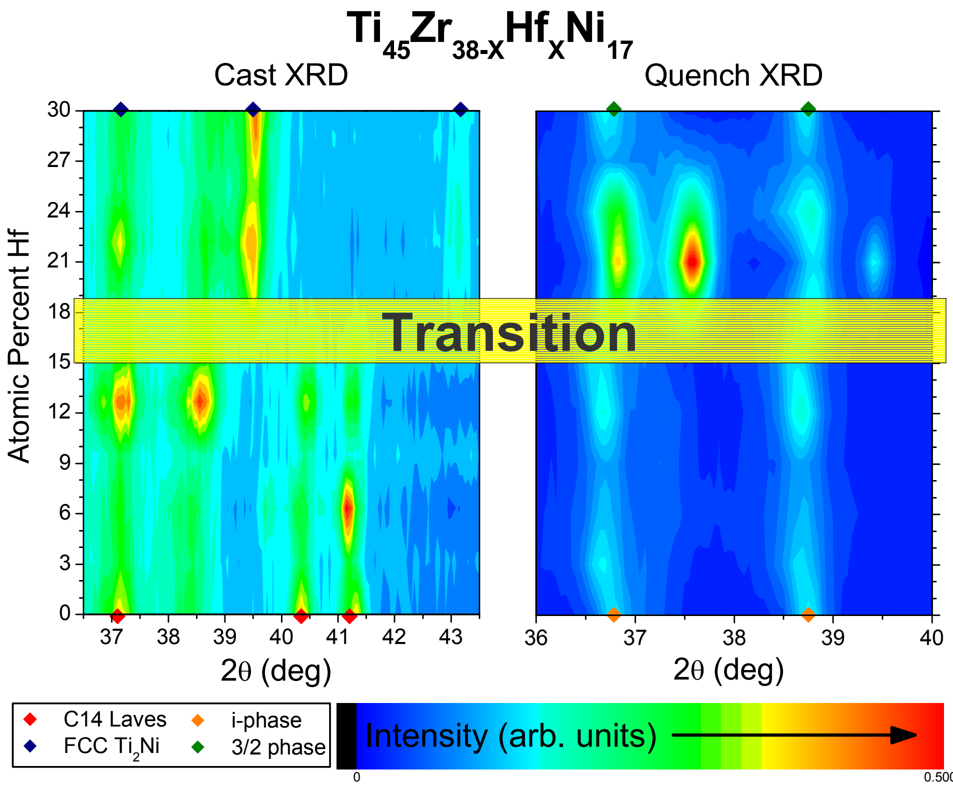


Figure 1 – X-ray diffraction intensity for a selected region of scattering angle as a function of Hf in as-cast (left) and rapidly-quenched (right) TiZrHfNi alloys. A narrow transition range in phase formation for both as-cast and quenched samples is indicated. *Results partially from undergraduate senior thesis research. of Josiah Hartzell.*

Outreach:

The PI is President of UCSAC, a science advisory council dedicated to improving science education in University City, MO, a racially and socio-economically diverse school system adjacent to Washington University. In October, he gave a public lecture entitled, “Atomic shuffle – the role of nucleation in the formation of materials.”

First Transparency

This gives an overview of our experimental proof of Frank's hypothesis in a TiZrNi alloy, demonstrating a growing icosahedral order with increased undercooling, and the preferential nucleation of a metastable icosahedral phase over a stable C14 Laves phase (which is also tetrahedral). That a fluctuation in order in the undercooled liquid determines the ordered phase that nucleates blurs the distinction between homogeneous and heterogeneous nucleation in this case. Further, such coupled ordering processes are not taken into account in the commonly used classical theory of nucleation.

<u>Bottom left</u> – Levitated TiZrNi liquid above the melting temperature.

<u>Top right</u> – Temperature of TiZrNi liquid measured as a function of time during free cooling. The sharp rise in temperature (recalescence) signals the nucleation and growth of the phases indicated (due to the release of the heat of fusion). The primary crystallization to the i-phase was confirmed by x-ray diffraction studies on the APS. That the i-phase transforms to the C14 phase approximately 2 seconds after its formation indicates that it is metastable, forming because the nucleation barrier is less.

<u>Bottom right</u> – Measured x-ray structure factors for levitated TiZrNi liquids as a function of decreasing temperature (liquidus is approximately 810^{o}C). The two arrows indicate a shoulder on the 2nd peak of S(q) which is becoming more distinct with decreasing temperature, indicating growing icosahedral order.

This work was reported in "First X-Ray Scattering Studies on Electrostatically-Levitated Metallic Liquids -- Demonstrated Influence of Local Icosahedral Order on the Nucleation Barrier," K. F. Kelton, G.W. Lee, A. K. Gangopadhyay, R. W. Hyers, T. J. Rathz, J. R. Rogers, M. B. Robinson, D. S. Robinson, Phys. Rev. Lett., **90**, 195504-1 – 195504-4 (2003).

An article describing this work, "Experiments vindicate a 50-year old explanation of how liquid metals resist solidification," appeared in the Search and Discovery section of the July, 2003 issue of Physics Today. The cover of that issue shows a levitated TiZrNi droplet in the ESL.

Second Transparency

This describes the educational aspects and outreach aspects of our research. Three undergraduate students Supported by REU funds for this grant are listed. The graduate and post-graduate participants are also listed.

<u>Right Figure</u> – this shows a topographic map of the x-ray intensity in a limited scattering angle range for TiZrHfNi alloys as a function of Hf concentration. As indicated by a band labeled "transition," both the as-cast and rapidly quenched samples show a transition in structure between 15 – 18 at.% Hf. In the as-cast alloys (labeled "Cast XRD") made with Hf concentration < 15 at.%, the primary crystal phase is a C14 hexagonal Laves phase (peaks indicated by the red diamond symbols at the bottom of the figure). For higher Hf concentrations, the primary crystallization phase is a Ti_2Ni fcc phase (peak locations indicated by the dark blue diamonds at the top of this figure). In the rapidly quenched alloys ("Quench XRD") with Hf concentration < 15 at.%, the two peaks near 37 and 39 degrees (indicated by the orange diamonds at the bottom of the figure) belong to the i-phase. There is a slight shift in position on going through the transition region, corresponding to the replacement of the i-phase by a 3/2 crystal approximant (peak positions indicated by green diamonds at the top of the figure). The two bright peaks near 37 and 38.5 degrees in the two panels index to the solid solution phase. The transition near the same concentration in both the as-cast and rapidly quenched samples suggests a shift in the local atomic configurations and could hold the clue to why no i-phase is found in the TiHfNi alloys, only the high order approximants. The TiHfNi alloys are of interest not only for their structure, but because they absorb large quantities of hydrogen with a reduced crystal hydride formation, over that in the TiZrNi quasicrystals. This work will form the core of a senior thesis for undergraduate Josiah Hartzell.